

# PATENT SPECIFICATION

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## (54) CATALYTIC PROCESS FOR MAKING POLYESTERS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1., a British Company do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the preparation of polyesters wherein the polycondensation stage is catalysed by the joint presence of a pentavalent antimony compound and a tin compound.

According to the present invention we provide a process for the preparation of a high molecular weight linear polyester by the polycondensation of a bis( $\omega$ -hydroxyalkyl) terephthalate using as polycondensation catalysts both a compound of antimony in the pentavalent state which is soluble in the reaction mixture and a compound of tin which is soluble in the reaction mixture.

The bis ( $\omega$ -hydroxyalkyl) terephthalate employed in the process of our invention may be prepared by any known method. In some modes of preparation of the bis ( $\omega$ -hydroxyalkyl) terephthalate there is a somewhat arbitrary distinction between the stage of preparation of the intermediate product and the start of the polycondensation stage and the addition of the antimony compound and/or the addition of the tin compound may be delayed until after some degree of polycondensation has been effected.

In the case wherein the preparation of bis ( $\omega$ -hydroxyalkyl) terephthalate involves an ester-interchange reaction, a suitable ester-interchange catalyst will normally be used in which case a phosphorus compound must be added at the end of the ester-interchange reaction in such an amount as to inhibit any adverse effect of the ester-interchange catalyst during the polycondensation stage. In that case the phosphorus compound must be of such type and in such quantity that no adverse effect is produced on either the antimony or the tin catalyst. For example, the insolubilisa-

tion of the antimony or the tin must be avoided. Preferably the phosphorus compound used should be an acid of phosphorus or an ester of such acid. Of particular value are phosphoric acid or an inorganic or organic phosphate. Examples of phosphorus compounds which we have found suitable are phosphorous acid, phosphoric acid, trimethyl phosphite, triphenyl phosphite, triphenyl phosphate, sodium dihydrogen phosphate, tris(dipropylene glycol) phosphonate, hydrogenated 4:4' - isopropylidene diphenol phosphite and tri(nonylphenyl) phosphite.

The quantity of antimony compound used as catalyst should be such as to correspond to at least 5 parts per million of antimony metal based on the bis( $\omega$ -hydroxyalkyl) terephthalate. The quantity of tin compound used as joint catalyst should be such as to correspond to at least 5 parts per million of tin metal based on the bis( $\omega$ -hydroxyalkyl) terephthalate. The relative quantities of the antimony and the tin compound should be such as to correspond to at least 0.5 atom of antimony to one atom of tin and may be as high as 30 atoms of antimony to one atom of tin. Advantageously the relative quantities should be such as to correspond to at least 1 atom of antimony to one atom of tin but not to be in excess of 10 atoms of antimony to one atom of tin. Particularly good results have been obtained by us when the relative quantities of the antimony and tin compounds were such as to correspond to from 1.3 to 5 atoms of antimony to one atom of tin.

Although the benefits of our invention are obtained when the antimony and tin compounds are each added at the same time and at any stage from the start of the preparation of the bis( $\omega$ -hydroxyalkyl) terephthalate, where appropriate this may be after some degree of polycondensation has been effected; either the antimony or the tin compound may be added first followed by the second compound. However, in such case it is preferable to add the antimony compound first.

In the term polyester we also include co-

polyester, the copolyester being prepared by modification of the process hereinbefore described according to known principles. The process of our invention is of particular utility in the manufacture of polyesters or copolyesters for the manufacture of fibres. For this application the copolyester molecule should preferably consist of at least 80% of units of a single alkylene terephthalate; the remaining structural units may, for example, be based on a second dicarboxylic acid, for example adipic or isophthalic acid, or a second glycol. Advantageously the alkylene terephthalate units are ethylene terephthalate.

Suitable antimony compounds for use in the process of our invention are, for example, antimoninic acid, antimony pentaglycoloxide, antimony pentoxide including hydrates of antimony pentoxide and potassium antimonate.

Suitable tin compounds for use in the process of our invention are, for example, stannous formate, stannous acetate, stannous octanoate, stannous oxalate, stannous chloride, stannic chloride, dioctyl thio tin, that is  $(C_8H_{17})_2SnS$ , dibutyl tin oxide, dibutyl tin acetate, dibutyl tin laurate, dibutyl tin maleate and tetrabutyl tin.

An advantage of the process of our invention is that by the use of it polyesters may be prepared using a short reaction cycle time and having visual appearance superior to that obtainable in the same reaction cycle time using pentavalent antimony compound alone, tin compound alone or trivalent antimony compound conjointly with tin compound.

Provided that it meets the above described requirements, a single compound may be used as the polycondensation catalyst, the single compound being both a compound of pentavalent antimony and a compound of tin.

A suitable temperature at which to carry out the polycondensation stage is between 250 and 350°C.

A fibre-forming molecular weight is above about 8,000, which corresponds to Viscosity Ratio 1.33 as measured at 1% in solution in orthochlorophenol at 25°C.

Other additives commonly present in polyesters may be added in the amount commonly used. Examples of such additives are phosphorus compounds, delustrants, optical whiteners and coloured materials.

Preferably the quantity of antimony compound present in the polycondensation reaction should not exceed that corresponding to 1,000 parts per million of antimony metal based on the bis ( $\omega$ -hydroxylalkyl) terephthalate and the quantity of tin compound present in the polycondensation reaction should not exceed that corresponding to 500 parts per million of tin metal based on the bis( $\omega$ -hydroxylalkyl) terephthalate.

In order that the nature of the process of our invention should be the more clearly understood, we give hereinafter Examples

3—7, 12—20, 22—26, 36—40, and 46—94, Examples 1, 2, 8, 9, 10, 11, 21, 27—35 and 31—45 are for comparative purposes. In all examples all parts are by weight.

A series of experiments was carried out using the following general method of procedure:

Dimethyl terephthalate (1552 parts) and ethylene glycol (1,235 parts) were reacted together under ester-interchange conditions in the presence of an ester-interchange catalyst. The reaction was carried out under reflux with final temperature 215—220°C, completion of reaction being judged by the evolution of approximately the theoretical quantity of methanol. The particular phosphorus compound used (if any) was then added and 5 minutes later titanium dioxide delustrant (7.76 parts) was added in the form of a slurry in ethylene glycol at 20% w/w concentration (except where otherwise stated). This was followed by the tin and antimony compounds, usually in that order except where indicated otherwise. These compounds were either pre-dissolved or slurried with ethylene glycol at 5.0% w/v concentration before addition. The tin and antimony compounds were added within 5 minutes of each other except where indicated otherwise. The resultant product was then transferred to a stainless steel autoclave and the temperature of the reactants raised to 290°C during 30 minutes, vacuum being applied from the time of attaining 235°C so that the pressure was less than 1 mm. of mercury 30 minutes after the start of application of vacuum. In cases where late addition is indicated, the addition was made when the pressure had reached 1 mm. of mercury. The polycondensation stage was judged to be complete when the power required to drive the agitator reached the value previously ascertained to correspond to the required molecular weight. The time taken for the polycondensation was counted from the earliest attainment of a temperature of the reactants of 285°C simultaneously with pressure falling below 1 mm. of mercury.

Intrinsic Viscosity (I.V.) was measured at 8% concentration (w/w) in orthochlorophenol at 25°C.

A superior visual appearance of polyester leads to superior fibre appearance. A measure of the superior visual appearance of the polyester is a high value for L—Y accompanied by a high value of L. L and Y refer to Luminance and Yellowness determined using a "Colormaster" differential colorimeter manufactured by the Manufacturers Engineering Equipment Corporation.

The antimoninic acid, used in some of the examples, had the composition  $Sb_2O_3 \cdot xH_2O$ . This was taken into account in calculation of parts per million (ppm) given in column 6 of Table 1 and column 7 of Table 2 and column 8 in Table 3, the parts per million being based

in the case of the ester-interchange route on the weight of dimethyl terephthalate charged and in the case of the esterification of terephthalic acid, on the weight of terephthalic acid.

5 In the Series A examples the phosphorus compound charged was  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$  used at 0.025% based on dimethyl terephthalate. The polycondensation catalysts were separately predissolved in glycol before charging.

10 In Series B examples the phosphorus compound charged was triphenyl phosphite used at 0.6% based on dimethyl terephthalate. The catalysts were predissolved in ethylene glycol and the solutions mixed before charging.

15 In series C examples the phosphorus compound charged was triphenyl phosphite used at 0.06% based on dimethyl terephthalate. The catalysts were each dissolved in ethylene glycol and the solutions mixed before charging.

20 In Series D examples the phosphorus compound charged was triphenyl phosphite used at 0.06% based on dimethyl terephthalate, except for example 30 wherein



25 was charged at 0.023% based on dimethyl terephthalate. The catalysts were each predissolved separately in ethylene glycol before charging.

30 In Series E examples the phosphorus compound charged was  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$  used at 0.025% based on dimethyl terephthalate. The catalysts were each predissolved separately in glycol before charging.

35 In Series F examples the phosphorus compound charged was  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$  used at

0.025% based on dimethyl terephthalate. In these examples either a tin or antimony compound was used as polycondensation catalyst alone and this was predissolved in glycol before charging.

In Series G the catalysts were predissolved separately in glycol before addition in all examples with the exception of Example 63 in which the stannic chloride and potassium antimonate were heated together in glycol until a clear solution was obtained.

In Series J, K, L, M, N, O, P and Q the catalysts were separately predissolved in glycol before charging.

In Example 82, the triphenyl phosphite was added after the catalysts, as opposed to the other examples.

In Example 88 no titanium dioxide de-lustrant was charged. In view of this it was not possible to carry out the measurement of Luminance and Yellowness since these would not be meaningful. The polyester produced was, however, clear and colourless.

In Example 89 titanium dioxide was charged in the amount to yield a polyester containing 2.0% of titanium dioxide.

In Examples 83, 84, 85 and 86, zinc acetate (0.12% based on dimethyl terephthalate) was used as ester-interchange catalyst. In Example 87, calcium acetate (0.07% based on dimethyl terephthalate) was used as ester-interchange catalyst. In all other examples involving ester-interchange, manganese acetate (0.025% based on dimethyl terephthalate) was used as ester-interchange catalyst. In each case the percentage is as the anhydrous salt.

TABLE I

Series	Example No.	Sn Compound	Sn ppm.	Sb Compound	Sb ppm	Sb/Sn atomic ratio	Polymerisation time (min.)	I.V.	L	Y	L-Y
A	1	SnOx	115	None	Nil	0	85	.662	74	41	33
	2	"	102	AA	50	.48	85	.659	75	35	40
	3	"	92	"	91	.97	62	.650	77	31	46
	4	"	86	"	117	1.33	67	.620	81	20	61
	5	"	57	"	254	4.35	76	.629	79	19	60
	6	"	48	"	292	5.9	71	.671	75	13	62
	7	"	29	"	351	11.8	65	.665	70	12	58
	8	"	13	"	409	37.6	85	.721	51	6	45
	9	None	Nil	"	468	∞	55	.657	66	14	52
B	10	Sn(Form) <sub>2</sub>	213	None	Nil	0	40	.655	69	58	11
	11	"	176	AA	87	.48	31	.662	74	43	31
	12	"	150	"	148	.97	34	.667	75	38	37
	13	"	138	"	177	1.25	38	.680	76	36	40
	14	"	116	"	229	1.93	43	.696	78	27	51
	15	"	94	"	280	2.9	47	.640	82	21	62
	16	"	75	"	326	4.25	55	.706	79	15	64
	17	"	68	"	335	4.8	46	.654	80	15	65
	18	"	61	"	424	6.8	47	.680	74	14	60
	19	"	41	"	406	9.7	42	.677	73	13	60
	20	"	16	"	467	28.4	51	.713	70	12	58
	21	None	Nil	"	504	∞	39	.697	68	18	50

TABLE I (continued)

Series	Example No.	Sn Compound	Sn ppm.	Sb Compound	Sb ppm	Sb/Sn atomic ratio	Polymerisation time (min.)	I.V.	L	Y	L-Y
C	22	DBTA	153	AA	159	1.01	38	.673	77	30	47
	23	"	116	"	236	2.0	50	.675	79	22	57
	24	"	87	"	236	3.7	43	.681	82	16	66
	25	"	51	"	371	7.3	47	.668	76	15	61
	26	"	44	"	438	9.7	51	.670	73	16	57
	27	SnAc <sub>2</sub>	112	None	Nil	0	50	.689	73	40	33
D	28	"	93	Sb <sub>2</sub> O <sub>3</sub>	210	2.2	50	.688	74	30	44
	29	"	74	"	285	3.75	55	.605	75	29.5	45.5
	30	SnOX	57	"	252	4.3	61	.641	77	27	50
	31	SnAc <sub>2</sub>	70	"	378	5.3	34	.680	78	27	51
	32	SnCl <sub>4</sub> 5H <sub>2</sub> O	74	"	378	4.99	40	.585	77	29	48
	33	SnAc <sub>2</sub>	42	"	462	10.7	45	.643	71	26	45
	34	"	23	"	504	21.3	59	.684	67	14	53
	35	None	Nil	"	504	∞	63	.696	58	2	56
	36	SnOx	35	AA	97	2.7	89	.674	80	22	58
	37	"	54	"	156	2.8	74	.596	81	20	61
E	38	"	69	"	195	2.8	65	.660	82	19	63
	39	"	98	"	280	2.8	63	.661	80	19	61
	40	"	115	"	325	2.8	49	.696	80	21	59
	41	SnOx	58	None	Nil	0	102	.648	79	28	51
F	42	"	115	"	"	0	85	.662	74	41	33
	43	None	Nil	AA	234	∞	80	.676	69	10	59
	44	"	"	"	325	∞	75	.708	68	12	56
	45	"	"	"	468	∞	55	.567	66	14	52

TABLE 2

Series	Example No.	P Compound	Sn Compound	Sb Compound	Sn ppm	Sb ppm	Sb/Sn atomic ratio	Polymerisation time (min.)	I.V.	L	Y	L-Y
G	46	.018 $\text{H}_3\text{PO}_4$	$\text{SnO}_x$	AA	58	234	3.9	61	.601	78	17	61
	47	.023 $\text{NaH}_2\text{PO}_4 \cdot \text{SH}_2\text{O}$	"	"	58	234	3.9	65	.723	79	19	60
	48	"	$\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$	"	51	234	4.5	72	.674	81	16	65
	49	"	$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$	"	58	234	3.9	64	.661	80	15	65
	50	.06 $\text{Ph}_3\text{PO}_4$	$\text{SnO}_x$	"	69	195	2.8	55	.670	82	16	66
	51	.015 PA	$\text{SnAc}_2 \cdot \text{H}_2\text{O}$	APGO	65	250	3.75	77	.685	81	15	66
	52	"	$\text{SnO}_x$	AA	69	195	2.8	70	.675	80	16	64
	53	"	$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$	"	68	195	2.8	66	.690	80	15	65
	54	"	$(\text{C}_6\text{H}_{17})_3\text{SnS}$	"	63	195	3.0	80	.630	79	22	57
	55	.06 TPP	$\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$	"	75	326	4.2	60	.660	79	14	65
	56	"	$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$	"	75	326	4.2	42	.655	81	16	65
	57	"	$\text{Sn}(\text{oct.})_2$	"	73	326	4.35	48	.679	80.5	15	66.5
	58	"	DBTO	"	81	326	3.9	51	.669	82	17	65
	59	"	DBTA	"	87	326	3.7	43	.681	82	20	62
	60	"	DBTL	"	69	326	4.6	49	.677	81	19	62
	61	"	DBTM	"	69	326	4.7	47	.669	81	22	59
	62	"	$\text{SnBu}_4$	"	70	326	4.5	54	.664	77	15	62
	63	"	$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$	$\text{KSb}(\text{OH})_6$	70	325	4.5	55	.660	77	13	64
	64	.024 TMP	$\text{SnAc}_3 \cdot \text{H}_2\text{O}$	AA	70	342	4.75	64	.666	79	18	61
	65	.09 TNPP	"	"	70	336	4.7	45	.650	81	17	64
	66	.09 HPDIPP	"	"	70	336	4.7	56	.700	79	13	66
H	67	.06 TPP	$\text{SnAc}_3 \cdot \text{H}_2\text{O}^*$	AA*	70	336	4.7	80	.707	78	17	61
	68	"	"	"	70	336	4.7	50	.649	80	16	64
	69	"	"	"	70	336	4.7	48	.660	79	16	63

TABLE 2—Continued

Series	Example No.	P % Compound	Sn Compound	Sb Compound	Sn ppm	Sb ppm	Sb/Sn atomic ratio	Poly- merisation time (min.)	I.V.	L	Y	L-Y
J	70	.1 TPP	"	AA	70	336	4.7	65	.646	78	21	57
	71	.025 H <sub>3</sub> PO <sub>3</sub>	"	"	70	336	4.7	77	.681	80	16	64
	72	.12 TPP.ate	"	"	70	336	4.7	69	.733	75	15	60
	73	.095 TPP.ate	"	APGO	70	325	4.5	77	.715	78	13	65
	74	.15 HPDIPP	"	AA	70	336	4.7	64	.720	76	15	61
	75	.015 HPDIPP	"	"	70	336	4.7	29	.670	81	23	58
K	76	.06 TPP	SnAc <sub>2</sub> .H <sub>2</sub> O	AA	23	48	2.0	98	.660	82	20	62
	77	.06 TPP	SnAc <sub>2</sub> .H <sub>2</sub> O	AA (1)	70	336	4.7	63	.664	75	36	39
L	78	"	SnAc <sub>2</sub> .H <sub>2</sub> O(1)	AA	70	336	4.7	76	.670	79	19	60
	79	.015 PA	SnOx	AA (1)	69	195	2.8	76	.686	74	34	40
	80	"	SnOx (1)	AA	69	195	2.8	58	.691	80	15	65
M	81	.1 TPP	SnAc <sub>2</sub> .H <sub>2</sub> O	AA	70	275	3.8	60	.665	78	22	56
	82	"	"	"	70	275	3.8	68	.645	79	22	57
N	83	.015 NaH <sub>2</sub> PO <sub>4</sub> .2H <sub>2</sub> O	SnOx	AA	69	195	2.8	75	.681	77	21	56
	84	.03 TPP	SnAc <sub>2</sub> .H <sub>2</sub> O	"	112	336	2.9	58	.693	74	16	58
	85	.033 TPP	"	APGO	74	275	3.6	79	.714	76	12	64
	86	.053 TNPP	"	"	70	325	4.5	53	.689	77	22	55
O	87	.15 TPP	SnAc <sub>2</sub> .H <sub>2</sub> O	APGO	70	325	4.5	56	.655	76	19	57
	88	.06 TPP	SnAc <sub>2</sub> .H <sub>2</sub> O	AA	70	305	4.25	50	.658			
P	89	"	"	"	70	305	4.25	56	.612	83	16	67

\* In Example 67 the polycondensation catalysts were slurried separately in glycol before charging.

Run	Monomer	Initiator	Temperature, °C	Time, hr	Yield, %	Viscosity, dl/g	Number-average molecular weight	Weight-average molecular weight	Comments
1	Styrene	BPO	100	2	100	0.45	10,000	20,000	Control
2	Styrene	BPO	100	2	100	0.45	10,000	20,000	Control
3	Styrene	BPO	100	2	100	0.45	10,000	20,000	Control
4	Styrene	BPO	100	2	100	0.45	10,000	20,000	Control
5	Styrene	BPO	100	2	100	0.45	10,000	20,000	Control
6	Styrene	BPO	100	2	100	0.45	10,000	20,000	Control
7	Styrene	BPO	100	2	100	0.45	10,000	20,000	Control
8	Styrene	BPO	100	2	100	0.45	10,000	20,000	Control
9	Styrene	BPO	100	2	100	0.45	10,000	20,000	Control
10	Styrene	BPO	100	2	100	0.45	10,000	20,000	Control
11	Styrene	BPO	100	2	100	0.45	10,000	20,000	Control
12	Styrene	BPO	100	2	100	0.45	10,000	20,000	Control
13	Styrene	BPO	100	2	100	0.45	10,000	20,000	Control
14	Styrene	BPO	100	2	100	0.45	10,000	20,000	Control
15	Styrene	BPO	100	2	100	0.45	10,000	20,000	Control
16	Styrene	BPO	100	2	100	0.45	10,000	20,000	Control
17	Styrene	BPO	100	2	100	0.45	10,000	20,000	Control
18	Styrene	BPO	100	2	100	0.45	10,000	20,000	Control
19	Styrene	BPO	100	2	100	0.45	10,000	20,000	Control
20	Styrene	BPO	100	2	100	0.45	10,000	20,000	Control
21	Styrene	BPO	100	2	100	0.45	10,000	20,000	Control
22	Styrene	BPO	100	2	100	0.45	10,000	20,000	Control
23	Styrene	BPO	100	2	100	0.45	10,000	20,000	Control
24	Styrene	BPO	100	2	100	0.45	10,000	20,000	Control
25	Styrene	BPO	100	2	100	0.45	10,000	20,000	Control
26	Styrene	BPO	100	2	100	0.45	10,000	20,000	Control
27	Styrene	BPO	100	2	100	0.45	10,000	20,000	Control
28	Styrene	BPO	100	2	100	0.45	10,000	20,000	Control
29	Styrene	BPO	100	2	100	0.45	10,000	20,000	Control
30	Styrene	BPO	100	2	100	0.45	10,000	20,000	Control
31	Styrene	BPO	100	2	100	0.45	10,000	20,000	Control
32	Styrene	BPO	100	2	100	0.45	10,000	20,000	Control
33	Styrene	BPO	100	2	100	0.45	10,000	20,000	Control
34	Styrene	BPO	100	2	100	0.45	10,000	20,000	Control
35	Styrene	BPO	100	2	100	0.45	10,000	20,000	Control
36	Styrene	BPO	100	2	100	0.45	10,000	20,000	Control
37	Styrene	BPO	100	2	100	0.45	10,000	20,000	Control
38	Styrene	BPO	100	2	100	0.45	10,000	20,000	Control
39	Styrene	BPO	100	2	100	0.45	10,000	20,000	Control
40	Styrene	BPO	100	2	100	0.45	10,000	20,000	Control
41	Styrene	BPO	100	2	100	0.45	10,000	20,000	Control
42	Sty								

## EXAMPLES 90-93

Terephthalic acid (1,328 parts) and ethylene glycol (775 parts in the case of Example 90 and 745 parts in the case of Examples 91, 92 and 93) were heated together (in the presence of sodium hydroxide where indicated) to a temperature of 230°C. and reacted with gradually rising temperature to final temperature 260°C. with periodical venting off of the water vapour formed by the reaction in order to maintain a total pressure of 40 pounds per square inch gauge. The total reaction time was 120 minutes. The temperature of the reaction mixture was then raised to 290°C. and the reaction continued under a pressure of 0.2 mm. of mercury. The degree of polycondensation was interpolated from the power re-

quired to drive the agitator and was judged to have reached the desired stage. The time for polycondensation is calculated from the point at which the pressure fell below 1 m.m. of mercury. In the Examples wherein a phosphorus compound is present, this was added at the end of the initial esterification before the pressure was reduced for the polycondensation stage.

The data for these Examples are given in Table 3 wherein the quantity of sodium hydroxide and of the phosphorus compound are expressed as a percentage based on the terephthalic acid charged. The parts per million of tin and of antimony are each expressed in the form of the metal referred to the weight of terephthalic acid charged.

TABLE 3

Series	Example No.	NaOH %	P % Compound	Sn Compound	Sb Compound	Sn ppm	Sb ppm	Sb/Sn atomic ratio	Polymerisation time (min.)	I.V.	L	Y	L-Y
Q	90	Nil	Nil	SnAc <sub>2</sub> .H <sub>2</sub> O	AA	82	395	4.7	58	.665	79	22	56
	91	Nil	.0058 H <sub>3</sub> PO <sub>4</sub>	SnOx	"	68	273	3.9	55	.674	78	22	56
	92	.0058	.015 PA	SnAc <sub>2</sub> .H <sub>2</sub> O	"	82	356	4.25	75	.714	76.5	19	57.5
	93	"	.044 TPP	"	"	82	391	4.7	88	.713	73	18	55



## NOTES ON TABLES

- (1) All recipe figures are percentages by weight on dimethyl terephthalate or terephthalic acid charged.
- (2) HIPDIPP = hydrogenated 4:4'-isopropylidene diphenol phosphite.
- (3) AA = Antimonic acid.
- (4) Ac = Acetate radical.
- (5) APGO = Antimony pentaglycoloxide.
- (6) Bu = Butyl.
- (7) DBTA = Dibutyl tin diacetate.
- (8) DBTL = Dibutyl tin dilaurate.
- (9) DBTM = Dibutyl tin maleate.
- (10) DBTO = Dibutyl tin oxide.
- (11) Form. = Formate radical
- (12) l = Late (in connection with late addition).
- (13) Oct. = Octanoate radical.
- (14) Ox. = Oxalate radical.
- (15) PA = Phosphorous acid.
- (16) P/C = Polycondensation.
- (17) Ph = Phenyl radical.
- (18) TMP = Trimethyl phosphite.
- (19) TNPP = tri(nonylphenyl) phosphite.
- (20)  $\text{Ph}_3\text{PO}_4$  = Triphenyl phosphate.
- (21) TPP = Triphenyl phosphite

## EXAMPLE 94

This demonstrates the preparation of a copolyester according to the process of our invention.

Dimethyl terephthalate (1,241 parts) and ethylene glycol (1,235 parts) were reacted together under ester-interchange conditions in the presence of manganese acetate tetrahydrate (0.551 parts) as catalyst. The reaction was carried out under reflux with final temperature 215—220°C., completion of reaction being judged by the evolution of approximately the theoretical quantity of methanol. After completion of ester-interchange, isophthalic acid (264 parts) was added and the temperature raised to 245°C. and reaction continued under a total pressure of 40 pounds per square inch gauge, the pressure being maintained by periodic venting off the water vapour pro-

duced by reaction. Reaction was complete in 30 minutes. The pressure was then released over 10 minutes. To the reaction mixture were charged triphenyl phosphite, tin acetate ( $\text{SnAc}_2 \cdot \text{H}_2\text{O}$ ) and antimonic acid, the quantity of each of the three being equivalent to that charged in Example 67, that is based on the weight of dimethyl isophthalate equivalent to the isophthalic acid charged the quantities were 0.06% of triphenyl phosphite, 70 parts per million of Sn and 336 parts per million of Sb. The resultant product was then transferred to a stainless steel autoclave and polycondensation carried out as described hereinbefore for the ester-interchange method.

The polymerisation time was 80 minutes giving a copolyester of Intrinsic Viscosity of 0.67, a Luminance of 72.5 and a Yellowness of 20. The ratio of Sb/Sn used was 4.7,

### Preparation of Antimony Pentaglycoloxide

Antimonic acid, with the approximate formula  $\text{Sb}_2\text{O}_5 \cdot 7\text{H}_2\text{O}$  or  $\text{HSb}(\text{OH})_6$ , was prepared from potassium antimonate  $\text{KSb}(\text{OH})_6$ .

- 5 The potassium antimonate (50 g.) was dissolved in 100 parts of water. To the solution was added 5M nitric acid (50 parts), slowly and with good agitation. The white precipitate formed was filtered off and washed free from nitric acid with water and dried in air at 25°C. until the free moisture content (measured by drying *in vacuo* at 25°C. for 24 hours) was less than 8%.

- 10 Within 48 hours of preparation, the antimonic acid (1 part) was dissolved by boiling under reflux in ethylene glycol (4 parts) for not more than one hour; water vapour was allowed to escape freely from the system during the heating up and refluxing. The solution was filtered at a little above 100°C. if necessary, and allowed to cool to 25°. The precipitation of solid white antimony pentaglycoloxide was then assisted by the addition of acetone equal in volume to twice that of the

solution. After allowing to stand for 6 hours, the solid precipitate was filtered under suction and dried *in vacuo* at 25° for 24 hours.

The product contained (50±5)%  $\text{Sb}(\text{V})$  (theoretical for  $\text{Sb}_2(\text{OCH}_2\text{CH}_2\text{O})_5 = 44.9\%$ ). The  $\text{Sb}(\text{III})$  content was below 0.5%.

### Preparation of Tin Acetate

30 g. black stannous oxide containing not less than 70%  $\text{SnO}_2$ , the remainder being substantially  $\text{SnO}$ , were added to 1,000 ml glacial acetic acid and the mixture was heated to the boiling point and boiled under reflux for 1 hour, water vapour and a little acetic acid vapour being allowed to escape. The hot liquor was then filtered on a preheated filter to remove solid material, and allowed to cool to 25°C. A creamy-white voluminous precipitate of tin acetate was formed. This was freed from acetic acid by filtration under suction and drying for 48 hours at 25°C *in vacuo*.

The dried solid tin acetate was analysed as shown in Table 4 (percentage composition).

TABLE 4

	Material prepared as described	$\text{Sn}(\text{OOCCH}_3)_2 \cdot \text{H}_2\text{O}$ theoretical
Sn	45.3	46.6
Acetic acid (by filtration)	47.7	47.1
C	19.4	18.9
H	2.65	3.1

- Up to 50% of the tin contained in the tin acetate product was in the stannic,  $\text{Sn}(\text{IV})$ , state.

Since the empirical formula is in agreement with the composition



- the tin acetate product is referred to hereinbefore as  $\text{SnAc}_2 \cdot \text{H}_2\text{O}$ , but the precise nature of the substance is uncertain.

### EXAMPLE 95

- A selection of the polyesters from the examples described hereinbefore, both according to our invention and outside of our invention were melt-spun at a spinning temperature of 287°C. through a spinneret bearing 20 holes of 9 thousands of an inch diameter using a wind-up speed of 4,200 feet per minute to give a spun denier of 157. This yarn was drawn at 2,500 feet per minute using a draw ratio of 3.22, over a hot roll at 90°C. and a hot plate at 170°C. Examination of the result-drawn yarns showed that the improved lumin-

ance and value for luminance minor yellowness of the polyesters according to our invention were maintained in the drawn yarns.

### WHAT WE CLAIM IS:—

1. A process for the preparation of a high molecular weight linear polyester by the polycondensation of a bis( $\omega$ -hydroxyalkyl) terephthalate using as polycondensation catalyst or catalysts either a compound containing pentavalent antimony and tin which is soluble in the reaction mixture or both a compound of antimony in the pentavalent state which is soluble in the reaction mixture and a compound of tin which is soluble in the reaction mixture, the quantity of antimony compound and the quantity of tin compound present being in each case sufficient to correspond to the presence of at least 5 parts per million of the metal based on the bis( $\omega$ -hydroxyalkyl) terephthalate and the quantities of antimony compound and of tin compound being such as to correspond to at least 0.5 atoms but not to exceed 30 atoms of antimony to one atom of tin.

2. A process according to Claim 1, wherein the quantities of antimony compound and of tin compound are such as to correspond to at least 1 atom but not to exceed 10 atoms of antimony to one atom of tin.
3. A process according to Claim 1 wherein the quantities of antimony compound and of tin compound are such as to correspond to at least 1.3 atoms but not to exceed 5 atoms of antimony to one atom of tin.
4. A process according to any of Claims 2 or 3 wherein the quantity of antimony compound present is such as to correspond to not more than 1,000 parts per million of antimony metal based on the bis( $\omega$ -hydroxyalkyl) terephthalate, and the quantity of tin compound present is such as to correspond to not more than 500 parts per million of tin metal based on the bis( $\omega$ -hydroxyalkyl) terephthalate.
5. A process according to any of Claims 1—4 wherein the antimony compound is antimoninic acid, antimony pentaglycoloxide, antimony pentoxide or potassium antimonate.
6. A process according to any of Claims 1—5 wherein the tin compound is stannous formate, stannous acetate, stannous octanoate, stannous oxalate, stannous chloride, stannic chloride, dioctyl thio tin, dibutyl tin oxide, dibutyl tin acetate, dibutyl tin laurate, dibutyl tin maleate or tetrabutyl tin.
7. A process according to any of Claims 1—6 wherein the polyester is a fibre-forming polyester.
8. A process according to any of Claims 1—7 wherein the polyester is a polyester of which at least 80% of its units are of a single alkylene terephthalate.
9. A process according to Claim 8 wherein the alkylene terephthalate is ethylene terephthalate.
10. A process according to any of Claims 1—7 wherein the polyester is poly(ethylene terephthalate).
11. A process for the preparation of a high molecular weight linear polyester according to Claim 1 as hereinbefore described with particular reference to the examples.
12. A high molecular weight linear polyester as prepared by the process claimed in any of Claims 1—11.
13. Fibres or filaments prepared from a polyester according to Claim 12.

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